



Influence of moisture absorption on properties of fiber reinforced polyamide 6 composites

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ABSTRACT

A state-of-the art study of thermoplastic polymer matrix materials for fiber composites has identified polyamide 6 (PA6) as a potential candidate thermoplastic polymer relevant for manufacturing large composite structures like wind turbine blades. The mechanical properties of PA6 are highly sensitive to moisture, and if PA6 is used as matrix material in a fiber composite, the properties of the fiber composite will depend on the moisture content of the material. At standard condition (23 °C and 50% RH) polyamide6 absorbs about 3 weight-% of water, whereas the PA6 material is dry right after manufacturing of components. In the current article, lamina properties of dry glass fiber/PA6 and conditioned (23 °C, 50% RH) glass fiber/PA6 are calculated for lamina with two different fiber content (45 and 50 vol.-%) by the use of classical micro mechanics. The matrix dominated properties like the shear stiffness, the shear strength and the stiffness and strength across the fiber direction are the ones which are mostly affected by the moisture content in the material.

INTRODUCTION

In the past 30 – 40 years fiber composites have been competing with materials such as steel, aluminum and concrete in cars, aircraft, buildings, bridges, bicycles and everyday sports goods. Glass fiber polyamide composites are among the fiber composites, which are of great interest to the automobile industries due to the considerable enhancement in properties like stiffness and strength, lower density, better process ability, compatible fiber availability with suitable sizing chemicals. Industries are entering the market with a new class of high-performance polyamides by modifying its chemistry and utilizing the benefits associated with the long glass-fiber-reinforced polyamides. In some applications, highly optimized short glass fiber-reinforced products reach their limitations, and then continuous glass fiber polyamides offer new opportunities. This shows a considerable advance in terms of performance of polyamides with the aim of metal substitution as the main objective in many industrial products.

Several researchers made significant efforts to investigate the material degradation of polymer composites under its exposure to extreme environmental conditions. One of the insidious disadvantages of certain polymers used in composites, such as polyamides is their tendency to absorb moisture from ambient, and then change their properties as an end result. The moisture may exist during different stages of polymer processing; it can be absorbed from surrounding atmosphere during storage and use. The moisture is known to affect a range of polymer properties, which in turn impact process ability, dimensional stability, mechanical, acoustic, electrical, optical, and chemical properties, as well as performance of the products [1].

Few research studies show that the tensile and transverse strength of composite resins demonstrate lower values after storage in water and test as compared to dry condition due to its water absorption [2]. Dimensional changes due to water absorption are much greater for highly hygroscopic thermoplastics, such as polyamides (PAs), and consequently affecting the overall performance [3]. The mechanical properties of PA6 are sensitive to moisture, and if PA6 is used as matrix material in a fiber composite, the properties of the fiber composite will depend on the moisture content of the material. For design of a large composite structure, it is realistic to use the mechanical properties of the glass fiber (GF)/PA6 in both dry and standard states. Right after manufacturing of a thick walled component it will have the properties of dry material, but after a couple of years at normal operating condition the material approaches the standard state.

In the present work, GF/PA6 laminate properties with 45 and 50% fiber volume fraction under dry and conditioned stages were evaluated theoretically using classical micro mechanics. The input data for the glass fiber and the PA6 material taken from various literature sources and data bases. The matrix dominated properties like the shear stiffness, the shear strength and the stiffness and strength across the fiber direction are the ones which are mostly affected by the moisture content in the material. For the conditioned material the stiffness across the fiber direction drops to about 1/3, whereas the other sensitive properties drop to about 1/2 of the properties for the dry material. The calculated properties are to be used as input data for design of a composite structures made by glass fiber/PA6 in order to evaluate, if the PA6 material can be used as a candidate as matrix material for final composite structures.

MOISTURE UPTAKE BY PA6

It is well known that polyamides (PA) absorbs relatively much moisture compared to other thermoplastic polymers and that the moisture content has a large influence on the properties (weight and mechanical) of the polyamides, which again will have an influence on the behaviour (strength, stiffness and natural frequency) of a large structures like wind turbine blade made in glass fiber/PA6. This article gives the lamina properties of dry glass fiber/PA6 and conditioned glass fiber/PA6 to be used as input data for design of a wind turbine blade in glass/PA6. The glass/PA6 is dry right after being processed. The conditioned glass/PA6 has a moisture content which is in equilibrium at 23 °C and 50% relative humidity (RH)).

The absorption of water in PA is slow at the standard condition (23 °C and 50% RH). The time for reaching equilibrium depends on the type of polyamide and the thickness of the component, but normally it takes months for thicknesses around 2-3

mm and years for thicknesses over 5 mm. However, accelerated conditioning can be used, as described in EN ISO 1110: “Plastics – Polyamides – Accelerated conditioning of test specimens”. The rate of moisture absorption is increased at elevated temperature, and one of the methods in the ISO standard is to condition the specimens at 70 °C and 62% RH. According to the ISO standard the equilibrium moisture content attained by this method is close to the equilibrium moisture content obtained in the standard atmosphere (23 °C and 50% RH). At standard condition (23 °C and 50% RH) PA6 absorbs about 3 weight-% of water [4]. (If the PA6 material is immersed into water it will be saturated with water, and the water content will increase to about 9 weight-%).

The mechanical properties of PA6 are sensitive to moisture, and typical values for dry and conditioned PA6 polymer [4] are given in Table I together with equivalent values for typical unsaturated polyester resin, for comparison. After processing PA6 polymer into components, the PA6 material is normally dry, where after uptake of water starts and the speed of uptake depends on the environment. Normally, the mechanical properties of a lamina made by PA6 polymer (i.e. a unidirectional fiber composite) are used as input data for designing of a wind turbine blade, but it has not been possible to find literature data for both dry and conditioned G/PA6 lamina.

Table I. Influence of water content on selected properties of polyamide 6

Property	Unit	PA6		Polyester
		Dry	Conditioned at 23 °C, 50% RH	(Typical type)
Tensile modulus	(MPa)	3400	1200	3500
Yield stress	(MPa)	90	45	50 – 80
Yield strain	(%)	10	> 50	3 – 6
Impact strength (Charpy notched)	(kJ/m ²)	4	50	15

LAMINA DATA (Classical micro mechanics)

As no full set of laminate data for G/PA6 was found in the literature, classical micro mechanics theory is used for calculation of the properties of the fiber composite lamina. All the calculations are performed by the use of the software program CompositPro®, [5]. Inputs for the calculations are properties of the fibers, properties of the matrix material and the fiber content. The fiber properties considered in this study are given in Table II.

Fiber properties

Table II. Typical properties of glass fibers

Property	Name and Units	E-Glass
Stiffness along the fibers	E_1 (GPa)	72.4
Stiffness across the fibers	E_2 (GPa)	72.4
Shear stiffness along the fibers	G_{12} (GPa)	30.3
Shear stiffness across the fibers	G_{23} (GPa)	30.3
Poisson's ratio (tension along fibers)	ν_{13}	0.20
Poisson's ratio (tension across fibers)	ν_{23}	0.20
Thermal expansion along fibers	CTE1 (mm/mm/C)	5.4E-06
Thermal expansion across fibers	CTE2 (mm/mm/C)	5.4E-06
Moisture expansion along fibers	CME1 (mm/mm/%m)	0.00E+00
Moisture expansion across fibers	CME2 (mm/mm/%m)	0.00E+00
Heat conductivity along fibers	K_1 (W/mK)	1.28
Heat conductivity across fibers	K_2 (W/mK)	1.28
Tensile strength along fibers	$+\sigma_1$ (GPa)	1.86
Compression strength along fibers	$-\sigma_1$ (GPa)	-1.10
Density	ρ_f (g/m ³)	2.6E+06

Matrix properties

The properties of dry and conditioned PA6 given in Table I are not sufficient as input data for CompositPro, and more data have been found in different references, calculated or estimated. The input values for CompositPro are listed in Table III.

Table III. Typical properties of dry and conditioned PA6

Property	Name and Unit	Dry	23 °C, 50% RH
Stiffness	E_m (GPa)	3.40	1.20
Shear stiffness	G_m (GPa)	1.26	0.44
Poisson's ratio	ν_m	0.35	0.35
Thermal expansion	CTE _m (m/m/C)	8.5E-05	8.5E-05
Moisture expansion	CME _m (m/m/%m)	3.3E-03	3.3E-03
Heat conductivity	K_m (W/m/K)	0.19	0.19
Tensile strength	$+\sigma_m$ (MPa)	90	45
Compression strength	$-\sigma_m$ (MPa)	-90	-45
Shear strength	$(\sigma_{12})_m$	72	36
Density	ρ_m (g/m ³)	1.13E+06	1.16E+06

Tensile strength and stiffness, coefficient of thermal expansion, heat conductivity and the density (only dry density) are taken from ref. [4].

Poisson ratio is taken from ref. [6].

Shear modulus is calculated as $G = E / (2(1+\nu))$ (1)

Compression strength is estimated to be the same as the tensile strength. In some references [7-8], it is stated to be a little less or the same, and in ref. [9] to be a little higher.

Shear strength is estimated to 80% of the tensile strength. It corresponds well to the values given in ref. [8-9]. If von Mises failure criterion is used the shear strength is only 58% ($1/\sqrt{3}$) of the tensile strength.

Density of PA6 does not change (or at least negligible) with change in moisture content in according to ref. [3]. However, in order to calculate the weight of a conditioned wind turbine blade based on the density of the composite material, the density for the conditioned PA6 is on purpose set to be 3% higher than the density of the dry PA6, as the moisture content is 3% at 23 °C and 50% RH. If the same (and the correct) density is used for the dry and conditioned fiber composite, 3% of the weight of the PA6 material used for the blade should be added in order to get the total weight of the blade.

Coefficient of moisture expansion (CME) is calculated based on information and measurements given in ref. [3]. If the moisture content is 3% and it is assumed that the density of the PA6 is constant, the CME can be calculated as follows, where L is length and M is mass:

$$\text{CME} = (\Delta L/L_{\text{dry}})/\% \text{-moisture} \quad (2)$$

$$(\Delta L/L_{\text{dry}}) = (L_{3\%} - L_{\text{dry}})/L_{\text{dry}} = L_{3\%}/L_{\text{dry}} - 1 = \sqrt[3]{(M_{3\%}/M_{\text{dry}})} - 1 = \sqrt[3]{1.03} - 1 = 0.0099$$

$$\text{CME} = 0.0099/3 = 0.0033 \text{ m/m/\%moisture}$$

G/PA6 properties (Dry and Conditioned)

Lamina data for both dry and conditioned G/PA6 are calculated for two fiber content, 45 vol.-% as well as 50 vol.-%, and the results are shown in Table IV. The fiber content in the load bearing laminate of a wind turbine blade depends on the manufacturing technique and the actual material system, but it is expected that the fiber content for a G/PA6 material will end up in the interval of 45-50 vol.-%.

As expected, it is the matrix dominated properties like the shear stiffness, the shear strength and the stiffness and strength across the fiber direction which are most affected by the moisture content in the material. For the conditioned material the stiffness across the fiber direction drops to about 1/3, whereas the other sensitive properties drop to about 1/2 of the properties for the dry material.

Table IV. Properties of dry and conditioned glass fiber/PA6 lamina ($V_f = 45$ and 50%)

Property	Symbol and Unit	Fiber content 45 vol.-%		Fiber content 50 vol.-%	
		Dry	23 °C, 50% RH	Dry	23 °C, 50% RH
Stiffness along fibers	E1 (GPa)	34.5	33.3	37.9	36.8
Stiffness across fibers (in-plane)	E2 (GPa)	9.43	3.53	10.4	3.94
Stiffness in thickness direction	E3 (GPa)	9.43	3.53	10.4	3.94
Shear stiffness in 1-2 plane	G12 (GPa)	3.04	1.13	3.41	1.28
Shear stiffness in 1-3 plane	G13 (GPa)	3.04	1.13	3.41	1.28
Shear stiffness in 2 - 3 plane	G23 (GPa)	3.53	1.31	3.91	1.46
Poisson's ratio (tension along fibers)	ν_{12}	0.283	0.283	0.275	0.275
Poisson's ratio (tension along fibers)	ν_{13}	0.283	0.283	0.275	0.275
Poisson's ratio (tension across fibers)	ν_{23}	0.433	0.459	0.412	0.435
Thermal expansion along fibers	CTE1 (mm/mm/°C) x 10^{-6}	9.72	6.98	8.97	6.70
Thermal expansion across fibers	CTE2 (mm/mm/°C) x 10^{-6}	0.633	0.641	0.582	0.588
Thermal expansion in thickness direction	CTE3 (mm/mm/°C) x 10^{-6}	0.633	0.641	0.582	0.588
Moisture expansion along fibers	CME1 (mm/mm/%m) x 10^{-3}	0.179	0.065	0.148	0.054
Moisture expansion across fibers	CME2 (mm/mm/%m) x 10^{-3}	2.40	2.43	2.19	2.21
Moisture expansion in thickness direction	CME3 (mm/mm/%m) x 10^{-3}	2.40	2.43	2.19	2.21
Tensile strength along fibers	+ σ_1 (MPa)	838.0	838.0	931.0	931.0
Tensile strength across fibers	+ σ_2 (MPa)	71.1	35.2	72.2	35.8
Shear strength in the plane	+ τ_{12} (MPa)	56.8	28.2	57.7	28.7
Compression strength along fibers	- σ_1 (MPa)	-497.0	-497.0	-552.0	-552.0
Compression strength across fibers	- σ_2 (MPa)	-71.1	-35.2	-72.2	-35.8
Shear strength in the plane	- τ_{12} (MPa)	-56.8	-28.2	-57.7	-28.7
Heat conductivity along fibers	K1 (W/mK)	0.682	0.682	0.737	0.737
Heat conductivity across fibers	K2 (W/mK)	0.361	0.361	0.394	0.394
Heat conductivity in thickness direction	K3 (W/mK)	0.361	0.361	0.394	0.394
Density	ρ (g/m ³)	1.79E + 06	1.81E+06	1.87E+06	1.88E+06

Table V. Mechanical properties – UD glass fiber/PA6 dry composites

Sl. No.	Material system	Fiber volume fraction V_f (%)	Compression modulus E^C (GPa)	Compression strength σ^C (MPa)	Compression strain to failure ϵ^C (%)	Inter-laminar shear strength ILSS (MPa)
Prepreg Laminate						
1	GF/PA6	47.0	34.6	534	1.6	59.3
Commingled Laminate						
2	GF/PA6	47.8	39.1	577	1.5	69.8
Reactive based polymers						
3	GF/APA6 [11]	50.0	26.0	473	1.9	---
Reference Laminate						
4	GF/Polyester	50	38	570	1.5	76

RESULTS AND DISCUSSIONS

The calculated glass/PA6 composite properties (Table IV) match reasonable well with the properties for the dry GF/PA6 composites given in Table V (compression modulus, inter-laminar shear strength and compression strength) both prepreg and commingled laminates. They match better with the properties for the conditioned material. Matrix dominated properties are mostly affected for conditioned samples. The lowering of mechanical properties of the conditioned samples could be attributed to the combined effects of temperature and moisture, i.e., hygrothermal effects. There is no experimental data in the present work to prove material degradation which could consider the data in Table V for dry laminate properties comparable with conditioned laminate property data sets.

A few studies in the literature like van Rijswijk et al. [10-11] prove that conditioned GF/PA6 laminate performances compared to dry laminates are degraded. The author considered epoxy, anionic polyamide 6 (APA6), and polyamide 6 materials to investigate the effect of moisture on glass fiber reinforced composites. The results prove significant property drop for the conditioned fiber composites compared to dry as manufactured samples. Similarly Selvam et al. [12] studied moisture and UV effect on liquid molded carbon fabric reinforced PA6 composites, where polyamide resin is a reactive based polymer called anionic polyamide, APA6. The authors [12] applied dual diffusivity model to evaluate the moisture uptake for the carbon fiber (CF)/APA6, fully immersed in the distilled water at 100 °C. The flexural strength is lowered by 45%, after exposure to moisture at 100 °C. The scanning electron microscope results show that moisture exposure result in surface micro-cracks compromising the fiber-matrix interface. UV exposure up to 600hrs causes the sample discoloration (yellowing of the samples) and an increase in crystallinity from 40% to 44%.

In the present work, both polished and unpolished cross sections are investigated at various magnification of optical microscope used to study the dry glass/PA6 composite to check the voids and porosities as shown in Figure 1. Very few and negligible defects are seen in the laminate micrographs such as tiny porosities as shown in the microscopic images Figures 1C, 1G, and 1H. The images shown in Figure 1A and Figure 1B has resin debond from fibers, which indicates weak interface bond between fiber and matrix material. The compressive failure surfaces and fiber-matrix interface, using scanning electron microscopes, are shown in Figure 2. Glass/PA6 show kink band failure under compression loading resulting in stepped failure of glass fibers. Comparison of compression strength values of different fiber reinforced polyamide6 composites such as dry and conditioned laminates are shown in Figure 3; the laminates made by glass fiber and APA6 has a big drop of strength values compared to other specimens made with PA6 polymer and with epoxy [10].

From the above discussion, it is noted that several researchers proved the matrix and fiber-matrix interface show appreciable damage after exposing to moisture, observed carefully by scanning electron microscopes. The polymer gets degraded initially and finally ending up with the composite performance degradation. This indicates that material degradation seen theoretically needs to be proved experimentally by performing several tests under various environmental conditions like exposed to moisture, UV radiation, and extreme conditions.

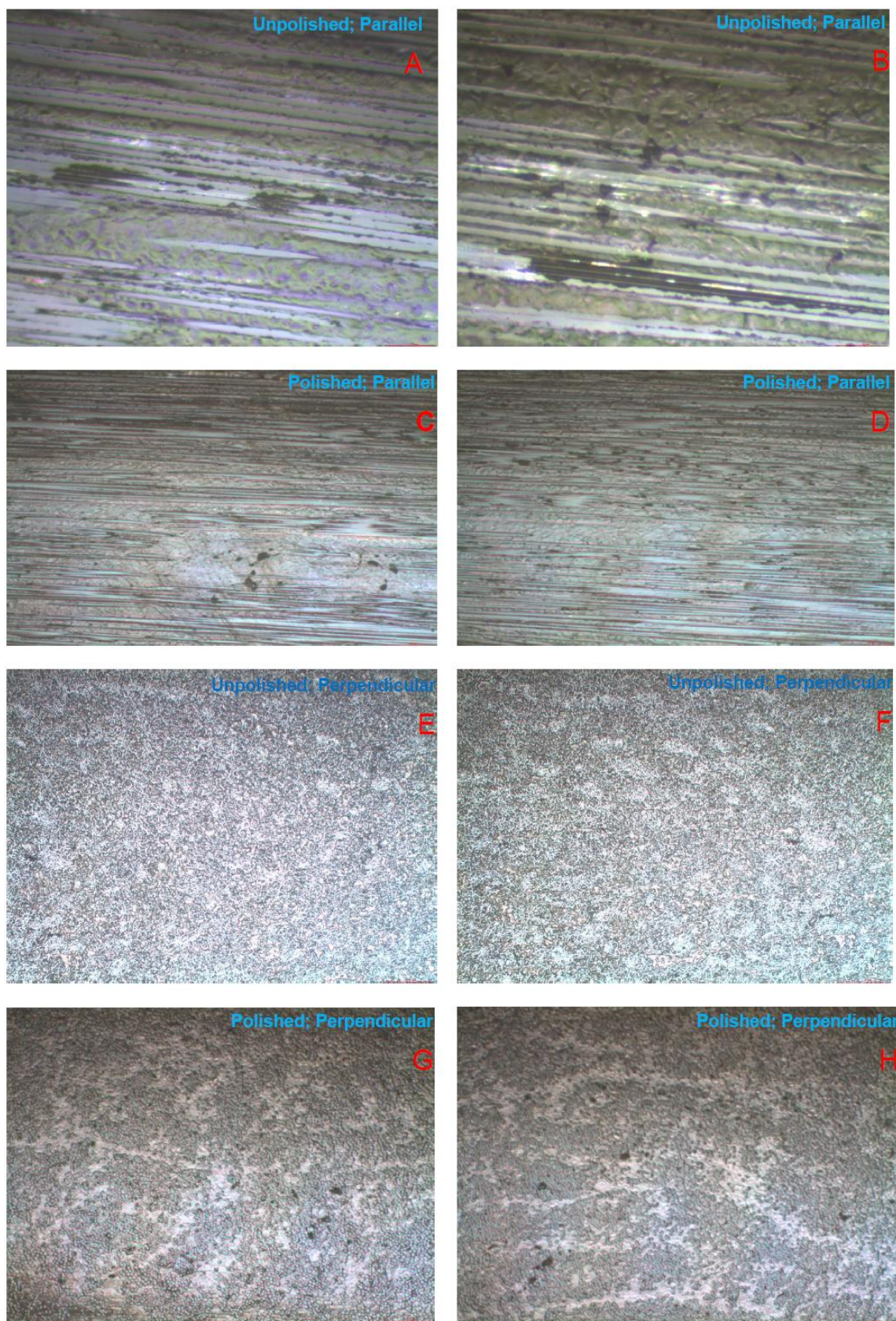


Figure 1. Glass/PA6 prepreg composite – 30 x optical micrograph [13]

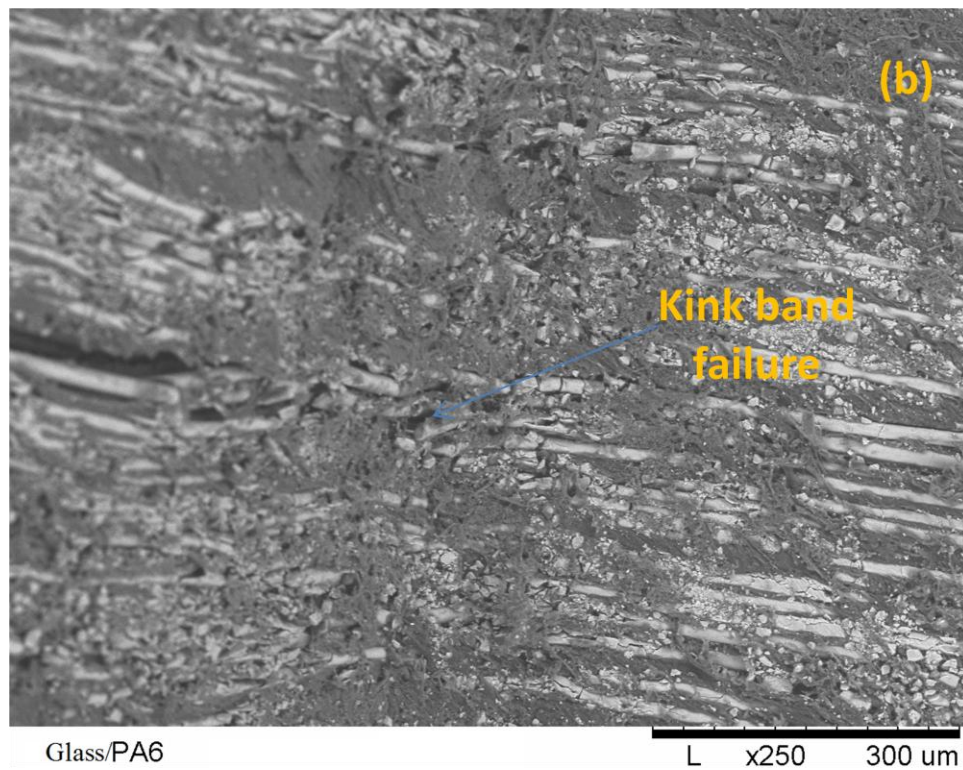
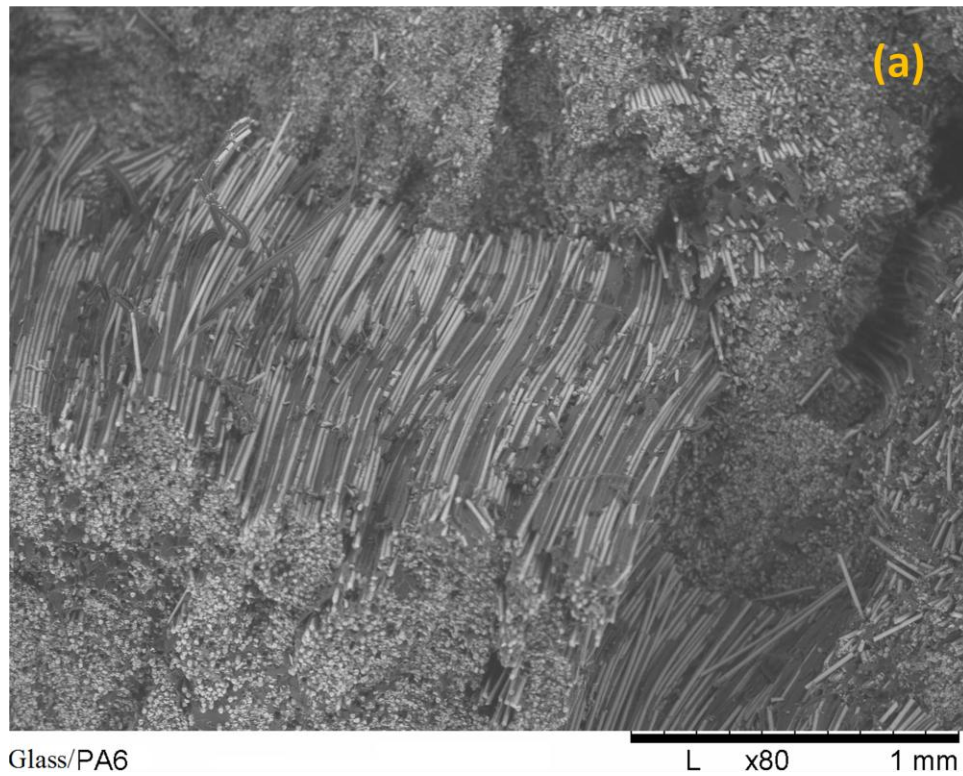


Figure 2. SEM of the compressive fracture surfaces of a dry glass/PA6 prepreg composite

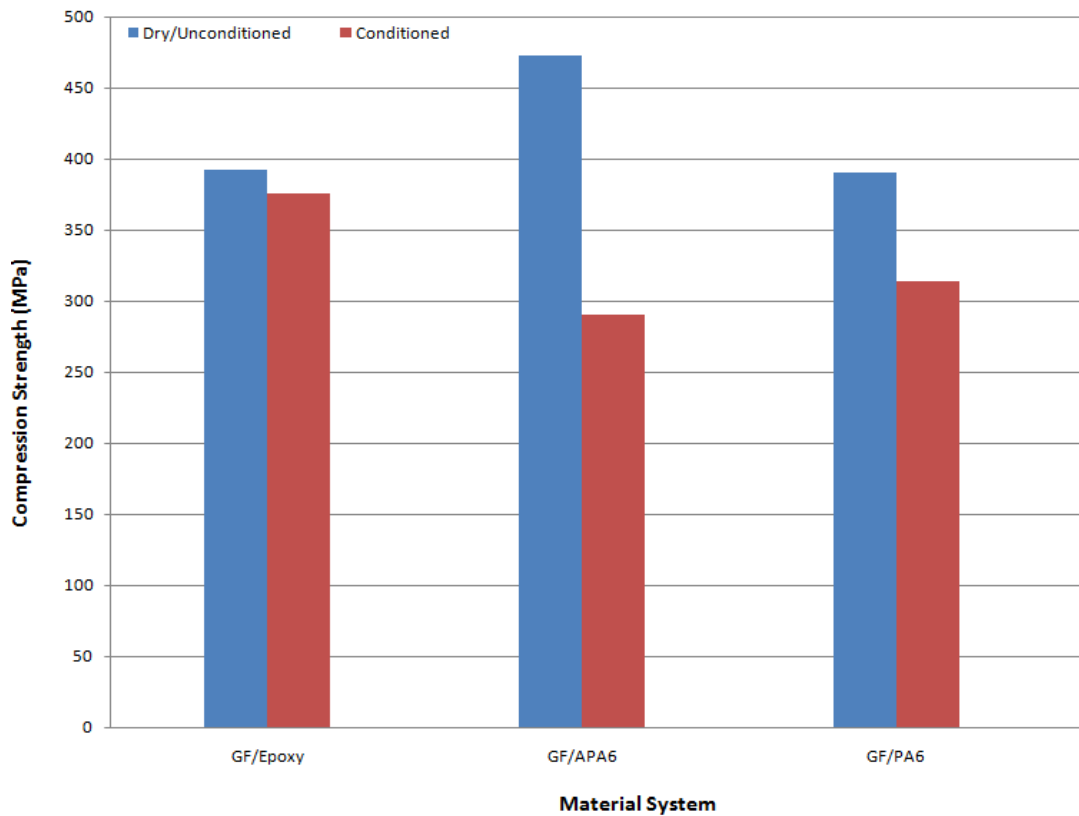


Figure 3. Strength variation of fiber reinforced PA6 composite both dry and conditioned specimens [11]

CONCLUSIONS

With the preliminary research study, it was possible to gain first important knowledge on environmental effect on material degradation based on laminate theory. The mechanical properties of PA6 are sensitive to moisture, and if PA6 is used as matrix material in a fiber composite, the properties of the fiber composite will depend on the moisture content of the material. At standard condition (23 °C, 50% RH) PA6 absorbs about 3 weight-% of water. The PA6 material is dry right after manufacturing of components, whereas the time for PA6 to reach the equilibrium moisture content at 23 °C and 50% RH depends on the thickness of the component, but normally it takes months for thickness around 2-3 mm and years for thicknesses over 5 mm.

Lamina properties are calculated using classical micro mechanics of dry and conditioned (23 °C, 50% RH) glass fiber/PA6 with two different fiber content (45 and 50 vol.-%) show matrix dominated properties like the shear stiffness, the shear strength and the stiffness and strength across the fiber direction are the ones which are mostly affected by the moisture content in the material. For the conditioned material the stiffness across the fiber direction drops to about 1/3, whereas the other sensitive properties drop to about 1/2 of the properties for the dry material. The calculated properties are to be used as input data for design of a wind turbine blade in glass fiber/PA6 in order to evaluate if the PA6 material is a candidate as matrix material for fiber composite wind turbine blades.

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